QUARTERLY PROGRESS REPORT
ON
CONFIGURATIONAL DIFFUSION OF
ASPHaltenES IN FRESH AND
AGED CATALYST EXTRUDATES

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Statement of Work

Configurational Diffusion of Asphaltenes in Fresh and Aged Porous Catalyst Extrudates

Objective: The objective of this research is to determine the relationship between the size and shape of coal and petroleum macromolecules and their diffusion rates i.e., effective diffusivities, in catalyst pore structures. That is, how do the effective intrapore diffusivities depend on molecule configuration and pore geometry.


Finite bath-type diffusion experiments will be performed using both coal and petroleum-derived macromolecular species, e.g. asphaltenes, as well as model compounds, e.g. porphyrins, polymers, of known molecular size. By monitoring the concentration of solute macromolecules in the bath, the effective intrapore diffusion coefficients will be determined through application of the appropriate diffusion equations. Macromolecular species concentrations will be monitored by size exclusion chromatography (SEC). Relationships will be sought between the size, and shape, e.g. planar, coil, of the diffusing solutes and the pore geometry (pore size distribution) of the catalyst support. The effects of molecule configuration and catalyst pore size distribution on the effective intrapore diffusivity will be examined. Specially prepared laboratory catalysts with very narrow pore size distributions and other model porous media, e.g. porous Vycor glass, will be utilized in the experiments. Pore structures of all catalysts and other porous media will be characterized by mercury porosimetry and surface area (BET) analysis.

Task 2. Effects of Solvent Composition, Solute Concentration, and Temperature on the Molecular Configuration and Diffusion Rate of Coal and Petroleum Asphaltenes in Catalyst Pores.
Diffusion experiments such as in Task 1 will be performed with varying solvent compositions, i.e., paraffinic-aromatic mixtures, to examine the effects of the state of molecular aggregation (self-assemblies) on the rates of diffusion of coal and petroleum asphaltenes in the catalyst pores. Similar experiments will be performed to study the effect of temperature and solute (macromolecule) concentration on the state of molecular configuration and aggregation on the resulting pore diffusivity.

**Task 3. Assessment of Diffusional Limitations in Aged Catalysts**

Diffusivity measurements such as conducted in Task 1 will be performed with both model compound and coal-derived macromolecular species using extrudate-type aged catalysts from laboratory experiments as well as aged catalysts obtained from actual coal liquefaction pilot plants such as the Wilsonville, AL Advanced Coal Liquefaction R & D Facility. From the experimental diffusivities so obtained, an evaluation of effects of changes in catalyst pore structure, e.g. tortuosity, pore plugging, shall be made. The changes in pore diffusivities associated with the pore structural changes caused by coke and metals deposition will be investigated, as compared with the fresh catalysts. As assessment of the relationship of increased diffusional limitations to coke and metals deposition in the catalyst pores will be made based on the results of the diffusivity measurements. The degree to which pore diffusivities can be restored to their original values by carefully controlled oxidation and/or extractive catalyst regeneration techniques also will be explored. The practical importance of these findings to coal liquefaction technology will be evaluated.
Summary

This quarter, adsorptive diffusion of both coal and petroleum asphaltenes in THF into porous catalysts were performed. A mathematical model with linear adsorption isotherm for asphaltene diffusion was developed. The molecular weight distributions of both asphaltenes were ascertained by GPC using polystyrene standards. The asphaltene diffusion data were simulated fairly well by the mathematical model, and linear adsorption constants were obtained for asphaltene fractions with different equivalent polystyrene molecular weights.

Planned Work

Next quarter, adsorptive diffusion experiments of asphaltenes in different solvents will be performed. The diffusion parameters will be ascertained by fitting the experimental data with a mathematical diffusion model. The effect of temperature on the behavior of diffusion as well as the stability of asphaltenes will be investigated.
Hindered Diffusion of Coal and Petroleum Asphaltenes

INTRODUCTION

Due to the comparability of the sizes of reactant molecules to those of catalyst pores, intrapore diffusion has been widely observed in the hydrotreatments of asphaltenes, heavy crudes, resids, coal derived liquids, and other macromolecular feeds (Ho and Weller, 1979; Eigenson et al., 1977; Song et al., 1991; Sooter and Crynes 1975; Yen et al. 1976; Kang, 1983; Guin and Curtis, 1883, 1984; Spry and Sawyer, 1975). Direct measurements of asphaltene intrapore diffusion in porous catalysts are recent and very few in number. Mieville et al. (1989) measured the diffusion of petroleum asphaltenes in toluene through porous materials by uptake experiments, in which the asphaltenes were treated as monodispersed and a linear adsorption isotherm was obtained. Several other studies on asphaltene diffusion were conducted with membranes. Among this line, Baltus and co-workers (Baltus and Anderson 1983, Baltus 1984, 1984a) studied hindered diffusion of petroleum asphaltenes through mica membranes. The asphaltenes were grouped into five regions with average molecular weights being defined by their elution characteristics from GPC (gel permeation chromatography). Their results showed that the experimental data could be well interpreted by hindered diffusion concepts. These studies have been continued by Kyriakou et al. (1988) and Nortz et al. (1990) with various fractionated samples of heavy oils by using polycarbonate membranes and Taylor-dispersion type experiments.

In this work, hindered diffusion of macromolecules was studied by the adsorptive uptake of coal and petroleum asphaltenes in THF from a finite bath surrounding a commercial NiMo/Al₂O₃
catalyst. The asphaltenes were grouped into several fractions, with molecular weights being determined by their elution characteristics on GPC. A diffusion model with linear adsorption was developed for each asphaltene fraction. The adsorptive diffusion parameters for the asphaltenes were ascertained by simulating the experimental data with the model solution.

EXPERIMENTAL

1. Materials

**Chemicals.** Two asphaltenes, one coal and one petroleum, were used in the diffusion study. The coal and petroleum asphaltenes were extracted from a coal resid and a petroleum asphalt, respectively. Detailed extraction procedure and properties of the sources were described in the last quarterly report. HPLC grade tetrahydrofuran (THF) was used as solvent in the diffusion experiments. Toluene and polystyrenes with narrow molecular weight distributions were used as calibration standards for analysis of asphaltenes on GPC (gel permeation chromatograph).

**Catalyst.** A commercial unimodal catalyst, Criterion 324, with an average pore diameter of 125 Å, was used in this study. Catalyst samples were crushed to -12+16 mesh size (-1.0+1.4 mm in diameter) and calcined at 673 K for 12 hours prior to use in diffusion experiments.

2. Apparatus and Procedures

**Diffusion Experiments.** Diffusion experiments were performed using the adsorptive uptake of asphaltenes in THF from a finite bath surrounding the catalyst pellets. Experiments were performed in a magnetically stirred glass diffusion cell containing a screen wire basket for holding catalyst particles at 308 K. Catalysts were presaturated with THF before diffusion runs, during which the
uptake of asphaltenes was monitored periodically by analyzing the concentration of asphaltenes in the bath solution using GPC.

**GPC Equipment.** A GPC (gel permeation chromatograph) device with a UV detector was used to analyze the concentration of asphaltenes in THF. The wavelength for the UV detector was chosen to be 262 nm. Four µ-styrage columns, with nominal pore sizes of 1000, 1000, 500 and 500 Å, were placed in series. A computer data acquisition system was employed to collect the UV absorbance of the effluent at a time interval of 2 seconds. HPLC grade THF was used as mobile phase with a flow rate of 1 cc/min. The THF reservoir was purged with He gas to keep THF from forming peroxides. Each asphaltene sample for GPC analysis was filtered before injection through a 0.1 µm syringe filter.

**HINDERED DIFFUSION MODEL FOR ASPHALTENES**

A mathematical model was utilized to describe the behavior of hindered diffusion of asphaltenes in porous catalyst particles. Due to the complexity, the asphaltenes are grouped into different fractions according to their molecular weights ascertained from GPC analysis. The porous catalyst particles were immersed in a finite well-stirred bath containing asphaltenes and solvent. The asphaltene molecules diffuse into the porous particle where they are adsorbed onto the solid catalyst surface. As a result of this diffusion-adsorption process, the concentration of asphaltenes in the surrounding bath is depleted. However, due to the difference in the adsorption capacity and diffusion rate of each asphaltene fraction, the depletion rates for the asphaltene fractions of different molecular weights will be different. The diffusion parameters of asphaltene fractions in the model can be determined by fitting a mathematical model to the experimentally observed uptake curves of the
fractions.

The hindered diffusion model developed here assumes negligible solute transport by surface diffusion, spherical catalyst particle geometry, uniform pore size distribution along the particle radius, negligible external fluid solid mass transfer resistance, and local adsorption equilibrium inside the particle pores. It is also assumed that the adsorption isotherm is linear for each fraction, and the properties of each fraction, such as the molecular size, the diffusivity, and the adsorption capacity, are independent of every other fraction during the adsorption-diffusion process.

With the above assumptions, the adsorption-diffusion mathematical model can be simplified and solved analytically, as shown before. The solution for dimensionless bath concentration of asphaltene fraction $j$ can be expressed as

$$\theta_y = \frac{B_j}{1+B_j} \sum_{k=1}^{3} \frac{\exp(-b_k^2 \gamma_j^2)}{b_k^2 b_k^2 + 9(1+B_j)}$$

where, the $b_k$'s are the non-zero roots of

$$\tan(b_k) = \frac{3b_k}{3+B_j b_k^2}$$

and

$$\theta_y = \frac{C_{y_j}}{C_{y_0}}$$

$$B_j = \frac{V_b}{V_p} \frac{1}{K_p e^{\rho_f K_f}}$$
\[ t_j = \frac{D_j}{R^2} \frac{1}{K_j e^{+D_j K_j}} t \]  

In above equations, \( K_j \) is the linear adsorption constant for fraction \( j \), and \( D_j \) is the effective diffusivity expressed as

\[ D_j = \frac{K_j e^D_j D_j}{\tau} \]  

in which \( e \) and \( \tau \) are catalyst porosity and tortuosity respectively, \( D_0 \) is the molecular diffusivity, \( K_{si} \) and \( K_0 \) factors are hindered diffusion parameters due to stearic and hydrodynamic factors, respectively.

For a hydrodynamic diffusion solute, the molecular diffusivity is related to the solute size by the Stokes-Einstein equation,

\[ D_0 = \frac{kT}{6\pi \eta_0 r} \]  

where \( \eta_0 \) is the solvent (THF) viscosity, being 0.442 cp or 4.42x10\(^{-3}\) g/cm-s at 35 °C, estimated via the following equation for THF (Reid, et al., 1977),

\[ \log (\eta_0) = 419.79 \left( \frac{1}{T} \right) \left( \frac{1}{244.46} \right) \]  

The two hindrance factors were estimated by the following two expressions derived for spherical solutes diffusing in cylindrical pores (Deen, 1987)

\[ K_{nj} = (1-\lambda_j)^2 \]
\[ K_j = 1 - 2.104 \lambda_j^2 - 2.089 \lambda_j^3 - 0.948 \lambda_j^5 \] (10)

For a typical adsorptive diffusion experiment, the values for most parameters in the mathematical model are known except those for \( K_j \) (or \( B_j \)) and \( D_j \). Therefore, the dimensionless bath concentration for each asphaltene fraction shown in equation (1) can be rewritten as,

\[ \theta_j = f(K_j, D_j, \phi, t) \] (11)

RESULTS AND DISCUSSION

1. Calibration of GPC Columns

GPC analysis of asphaltenes requires the use of calibration standards to determine the average molecular weights of the fractions from elution volumes. Studies have shown that a linear calibration curve obtained from polystyrene standards gives reasonable approximate values of the molecular weights of asphaltene fractions. Thus a calibration curve was obtained by the use of toluene and some polystyrenes with narrow molecular weight distributions as calibration standards.

Toluene and polystyrene standards with weight average molecular weights ranging from 500 to \( 5 \times 10^4 \) were first dissolved in THF, each with concentration of 1 mg/cc. The solutions of polystyrene (toluene)/THF were analyzed via GPC, and the logarithm of molecular weights of the standards vs. elution volumes is shown in Figure 1. It can be seen that a good linear fit of \( \log(M_w) \) vs. elution volume is obtained as,
\[ \log(M_w) = -0.125 V_p + 7.261 \] (12)

Figure 2 shows GPC chromatograms of coal and petroleum asphaltenes in THF. There are two x-axes in this figure, one is the elution volume, the other is the equivalent polystyrene/toluene molecular weight calculated from equation (12). From this figure it can be seen that the equivalent molecular weights of the coal asphaltenes, 50-1000, are much smaller than those of the petroleum asphaltenes (300-10000). In the simulation of experimental asphaltene diffusion data, several fractions of the asphaltenes will be defined in terms of the equivalent eluted polystyrene/toluene molecular weights. No attempt was made to determine the actual molecular weights of the various asphaltene fractions.

2. Estimation of Effective Diffusivities of Asphaltene Fractions

As discussed in the model development section, to do the simulation for each asphaltene fraction, the adsorption parameter \(K_j\) or the effective diffusivity \(D_{ej}\) should be known. Due to the stability of asphaltenes in solvent, it is difficult to obtain the linear adsorption constant \(K_j\) because of the longer time required for the equilibrium to be reached. On the other hand, if we can estimate the effective diffusivity for each asphaltene fraction, the adsorption parameter \(K_j\) can be ascertained by simulating the experimental data with the mathematical model.

As shown in equations (6-10), both \(K_{pp}\), \(K_j\) and \(D_{ej}\) therefore the effective diffusivity \(D_{ej}\) are related to the molecular size of each asphaltene fraction. Thus it is required that the size of the asphaltenes be known. Nortz et al. (1990) measured hydrodynamic properties of fractionated Athabasca tar sand bitumen vacuum bottoms and a blend of vacuum resid from Western Canada.
regressing the experimental data, they obtained the following relationship between the molecular radius and weight for the heavy oil fractions in THF,

\[ r = 0.36 \ MW^{0.50} \ \text{Å} \]  \hspace{1cm} (13)

in which the molecular weight of each fraction was determined by vapor pressure osmometer, and the molecule radius was calculated from the Stokes-Einstein equation with the molecular diffusivity being experimentally determined by the Taylor dispersion measurements.

We adopt the above equation to estimate the molecular size of our coal and petroleum asphaltenes in THF, even though the heavy oils Nortz et al. used may be different from the asphaltenes in this study. We also assume that the molecular weights of each coal and petroleum asphaltenes can be well represented by the polystyrene equivalent molecular weights via. GPC. With these assumptions, the effective diffusivities of asphaltenes fractions with different GPC elution volumes can be estimated from equations (6-10, 13). The results are shown in Table 1. It should be pointed out that a tortuosity value of 3.0 was chosen for the NiMo/Al\textsubscript{2}O\textsubscript{3} catalyst, which is reasonable for the catalyst of this type. Comparison of the results shown in Table 1 and Figure 2 shows that the molecular diffusivities for fractions of petroleum and coal asphaltenes are in ranges of 1.1 to 7.7x10^{-6} and 2.6 to 18x10^{-6} cm\textsuperscript{2}/s, respectively, with the corresponding effective diffusivities being in ranges of 3.5x10^{-9} to 1.1x10^{-6} cm\textsuperscript{2}/s and 1.4x10^{-7} to 3.3x10^{-6} cm\textsuperscript{2}/s.

3. Simulation of Asphaltene Diffusion into Porous Catalyst

In diffusion study, both the coal and petroleum asphaltenes were used as solutes. Figures 3 and 4 show the uptake data for the two asphaltenes in THF from Criterion 324 catalyst, respectively.
It can be seen from these figures that, as diffusion time increases, the UV absorbances or concentrations of both the coal and petroleum asphaltenes in the bath solution decrease. However, the decreasing rates for asphaltene fractions with different equivalent molecular weights are different, depending on their diffusion rates and adsorption capacities.

As discussed before, given the value of the effective diffusivity for each asphaltene fraction, the adsorption parameter $K_j$ can be obtained by simulating the experimental data with the mathematical model solution. In the simulation of the uptake data for the coal and petroleum asphaltenes in Figures 3 and 4 respectively, we first group the GPC data into several fractions, each with an elution time interval of 50 seconds or elution volume of 0.83 cm$^3$. The estimated effective diffusivities for these fractions are shown in Table 1. Figure 5 shows the simulated values of adsorption constant $K$ for different asphaltene fractions. It is interesting, as shown in Figure 5, that even though the properties of coal and petroleum asphaltene are much different, the simulated values of adsorption parameters for the fractions have the same trend; with increasing the equivalent molecular weight, the linear adsorption constant monotonically increases. A best fit with a second order polynomial can be obtained from the data points in Figure 5, as shown in the following equation,

$$K = 29.1 + 0.132 MW + 6.44 \times 10^{-5} MW^2 \quad (14)$$

As long as the relationship between the linear adsorption constant $K$ and the equivalent molecular weight is determined, the diffusion equation (1) can be solved for any fraction of asphaltenes. Figures 6 and 7 show the experimental uptake data together with the model solution for coal and petroleum asphaltenes, respectively. It is observed that for the coal asphaltenes, the model
fits experimental data well, as shown in Figure 6. For the petroleum asphaltene fractions with smaller equivalent molecular weights, the model fits experimental data fairly well, however, for the larger molecular weight region, some departure was observed, particularly at longer diffusion time.
**Table 1. Estimated effective diffusivities and other parameters**

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a. Determined by equation (13)
b. Estimated from equation (12)
c. Calculated from equation (7)
d. Determined by equation (6)
REFERENCES


Figure 1 Calibration of GPC columns by polystyrenes

\[
\log(MW) = -0.125V_e + 7.261
\]
Figure 2 Comparison of GPC molecular weight distributions in THF for coal and petroleum asphaltenes
Figure 3  Uptake of diffusion of coal asphaltenes in THF from Criterion 324 catalyst at 35 °C
Figure 4 Uptake of diffusion of petroleum asphaltenes in THF from Criterion 324 catalyst at 35 °C
Figure 5 Relationship between equivalent polystyrene molecular weight and linear adsorption constant $K$ for both coal and petroleum asphaltenes.

$$K = 29.1 + 0.132\times MW + 6.44\times10^{-5}\times MW^2$$
Figure 6 Simulation of experimental data with mathematical model for diffusion of coal asphaltenes in THF from Criterion 324 catalysts at 35°C
Figure 7 Simulation of experimental data with mathematical model for diffusion of petroleum asphaltenes in THF from Criterion 324 catalyst at 35 °C